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Electrophilic Amination of Aromatics with Sodium Azide in BF_3-H_2O

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ABSTRACT

Abstract: Boron trifluoride monohydrate is an excellent Brønsted acid catalyst system for a wide range of reactions. It is a non-oxidizing acid catalyst prepared easily by bubbling BF_3 into water. We have found boron trifluoride monohydrate/sodium azide combination to be an efficient reagent system for aromatic electrophilic amination. The present method avoids the use of expensive superacids such as trifluoromethanesulfonic acid and provides a facile access to aromatic amines directly from aromatics.

Introduction

Boron trifluoride was first prepared by Gay-Lussac and Thenard[1] in 1809 and since then, chemists have explored the remarkable propensity of this Lewis acid to form coordination compounds with a variety of Lewis n-donor bases such as water and alcohols in giving rise to strong conjugate Brønsted acid systems.[2] Unlike the other boron trihalides, boron trifluoride resists hydrolysis to boric acid and combines readily with water, resulting in highly acidic Brønsted acid solutions, the strength of which depends on the amount of water present.[3] Meerwein and collaborators[4] found that boron trifluoride forms stable monohydrate and dihydrate complexes which they prepared, characterized, and showed to be highly ionized in the liquid state.[5] Boron trifluoride dihydrate, BF_3-$2H_2O$, exists in the liquid state predominately as the ionic form, $[H_3O]^+[BF_3OH]^-$, has a Hammett acidity of H_o = -6.85 which is of the same order of acidity as that of 100% nitric acid.[3-4] The monohydrate complex BF_3-H_2O is an equivalent of $[H]^+[BF_3OH]^-$ with a reported Hammett acidity of H_o = -11.4,[5] and significantly more acidic than the dihydrate complex, its acidity being similar in strength to that of anhydrous sulfuric acid.[3-4] Farcasiu and Ghenciu[3c] have investigated the Hammett acidity of boron trifluoride-water complexes and found that boron trifluoride monohydrate to be a superacid with H_0 < -14. Boron trifluoride monohydrate is a colorless fuming liquid with a density of 1.8 g mL^{-1} and a melting point of 6.2 °C.

With a Hammett acidity value (H_o) of -14.1, triflic acid (trifluoromethanesulfonic acid, CF_3SO_3H) is a superacid according to the widely accepted definition of superacids by Gillespie[6] that acids having an $H_0 \leq -12$ are considered superacids. Triflic acid has, in general, been the superacid of choice in studying acid catalyzed reactions that proceed by superelectrophilic activation. However, a major drawback of triflic acid is its expense, which limits the opportunity to conduct many of these novel transformations on a larger scale. In contrast, BF_3-H_2O can be conveniently and inexpensively prepared in the laboratory by simply bubbling boron trifluoride gas in water with cooling and can be stored at -20 ^oC in Nalgene® bottles for more than a year without appreciable loss of activity. Its H_0 value of somewhere between -11.4 to -14.1 qualifies it as a superacid as well. Like triflic acid[7], boron trifluoride monohydrate is non-oxidizing in nature which can be critically important when dealing with substrates that are sensitive to oxidation.

Consequently, boron trifluoride monohydrate has been described in the literature as an efficient and inexpensive acid catalyst in comparison to expensive superacids such as triflic acid in a variety of organic transformations. It has been used in the oligomerization of 1-alkenes,[8] alkylation of aromatics with alkenes,[9] the Koch-Haaf carbonylation of alkenes or alcohols to carboxylic acids,[10] the Ritter reaction of alkenes to formamides,[11] deuteration of activated aromatics and polycyclic aromatics using BF_3-D_2O,[12] and the ionic hydrogenation of polycyclic aromatics,[13] aromatic organosulfur compounds[14] and disubstituted naphthalenes[15] in the presence of triethylsilane and also in the presence of catalytically active hydrogen.[16]

Owing to our interest in developing acid catalyzed methodologies, We have reported the utility of boron trifluoride monohydrate in the thioacetalization of ketones and aldehydes with 1,2-ethanedithiol,[17a] one-flask preparation of sulfides from carbonyl compounds with thiols and triethylsilane,[17b] the nitration of aromatics with either potassium nitrate or nitric acid,[17c] the 2,2,2-trifluoro-1-(ethylthiol)ethylation of aromatics with trifluoroacetaldehyde hydrate and ethanethiol,[17d] and the preparation of nitrite free alkyl nitrates from alcohols.[17e] Our group has also applied BF_3-H_2O in the preparation of symmetric bisulfides via reductive thiolation of dicarbonyls with thiols or of carbonyl compounds with dithiols, [18a] electrophilic halogenations of arenes with N-halosuccinimides,[18b] the Fries rearrangment,[18c] and hydroxyalkylation of arenes with pyridinecarboxaldehydes and quinolinecarboxaldehydes to form diaryl- methylpyridines and diarylmethylquinolines, [18d] hydroxyalkylation of arenes with benzaldehyde, and dialdehydes to form triarylmethanes, triarylmethane aldehydes and anthracenes, [18e] synthesis of 1,1,1-trifluoro- and 1,1-difluoro-2,2-diarylethanes from arenes and fluorinated hemiacetals, [18f] and condensation of aryldiamines with ketones to form perimidine and 1,5-benzodiazepine derivatives.[18g] Figure 1 shows selected BF_3-H_2O catalyzed reactions that our group has investigated over the years.

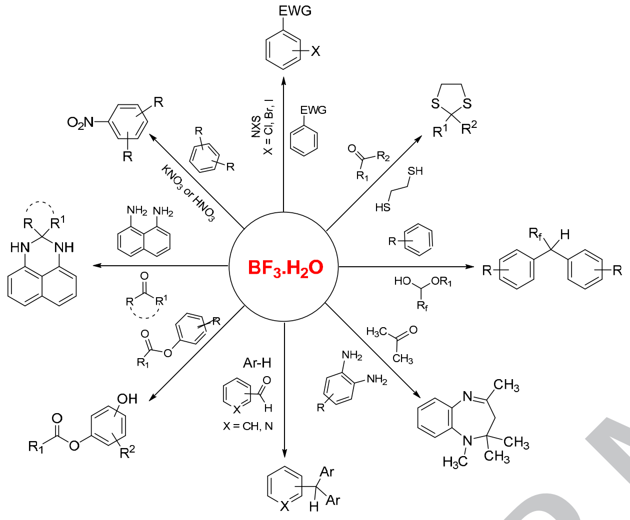


Figure 1. Selected reactions catalyzed by BF_3-H_2O

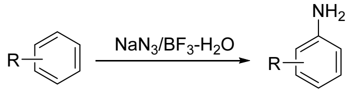
Aromatic amines are synthetically valuable intermediates. Aniline, the simplest of the aromatic amines, was discovered in 1826 by Otto Unverdorben. In 1856, William Henry Perkin discovered the first aniline dye, Mauveine. Since their initial use as precursors to dyes, aromatic amines have found widespread use in pharmaceuticals, agrochemicals, polymers etc.[19] Commercially, primary aromatic amines are prepared via nitration of aromatics followed by hydrogenation of nitroarenes over metal based catalysts.[20] They can also be prepared by nucleophilic aromatic substitution of haloarenes with ammonia.[21] Coupling aryl triflates with primary amides in the presence of a palladium-BINAP-$CsCO_3$ catalyst system also furnishes primary aromatic amines.[22] Recently, several methods have been reported wherein primary aromatic amines are obtained via electrophilic amination of aryl boronic acids.[23]

The simplest of the synthetic methods for the preparation of primary aromatic amines, however, would be direct amination of aromatic compounds. Many of the single-step production of primary aromatic amines via the direct amination of aromatics have focused on the use of gaseous ammonia as the aminating agent. However, the strength of the N–H bond in ammonia (107 kcal mol^{-1}) makes the "N–H activation" challenging.[24] Therefore, noble-metal and transition-metal catalysts and rigorous reaction conditions (high temperature and high pressure) are required to activate the N-H bond of gaseous ammonia.[25] Moreover, the yield of aniline in these studies is very low, even at high temperatures and high pressures. For example, the yield of aniline from benzene by the use of gaseous ammonia is 1.21 % at 450 K and 5 MPa in the presence of 0.5% Ru/Al_2O_3.[25a]

Hydroxylammonium chloride is another aminating agent that has been used for the direct electrophilic amination of aromatics in the presence of Friedel-Crafts catalysts.[26] Other reagents such as hydroxylamine and its salts,[27a] alkylhydroxylamines,[27b] hydroxylamine-O-sulfonic acid,[27c,d] and hydrazoic acid (HN_3).[27e] have also been used for amination of aromatics.

Schmidt was the first obtain aniline from benzene by sodium azide in concentrated sulfuric acid, albeit in low yield.[28a] Hoop and Tedder found that solutions of sodium azide in concentrated sulfuric acid were able to aminate a wide variety of aromatic nuclei, but the yields of amines were very low.[28b] They concluded that except with mesitylene, which gave a mixture of mesidine, diaminomesitylene and 3-amino-2,4,6-trimethylbenzenesulfonic acid, solutions of hydrazoic acid in sulfuric acid have little value as aminating agents. Kovacic and co-workers compared the reaction of hydrazoic acid with toluene in presence of sulfuric acid and aluminum chloride and found that aluminum chloride gave higher yield of toluidines.[27e] Olah and co-workers were able to show by NMR spectroscopy[28c] that protonation of hydrazoic acid and methyl or ethyl azides with superacids FSO_3H/SbF_5, HF/SbF_5, or HF/BF_3 results in the formation of stable aminodiazonium ions. The aminodiazonium ion was also prepared in situ from $(CH_3)_3SiN_3/HF/BF_3$ or $(CH_3)_3SiN_3/A1C1_3/HC1$ or $NaN_3/A1C1_3/HCl$ and the latter two systems were utilized in the direct amination of aromatics. Later, Christe and coworkers were able to isolate aminodiazonium ($H_2N_3^+$) salts of SbF_6^-, AsF_6^-, and BF_4^- from HF solutions of hydrazoic acid and the corresponding Lewis acids. [28d] Olah and co-workers subsequently reported[28e] trimethylsilyl azide/triflic acid as a highly improved reagent system that allowed simple and efficient direct amination of aromatics via aminodiazonium ion intermediate. With phenyl azide/triflic acid, the reactive intermediate is phenylaminodiazonium ion, making the system a powerful phenylaminating agent for aromatics to give the corresponding diarylamines.[28f] Primary aromatic amines can also be obtained from the reaction of hydrazoic acid with aromatics in presence of both trifluoromethanesulfonic acid (TFSA) and trifluoroacetic acid (TFA).[28g] However, the use of an excess amount aromatic compounds and low reaction regioselectivity are the drawbacks of these methods. Moreover, the yields are based on the aminating agent and not on the aromatic substrates to be aminated. Borodkin and co-workers[29] have reported direct one step amination of aromatics by using NaN_3/triflic acid/aromatics in a molar ratio of 1:3:1. However, the reaction was successful only in the case of very active substrates such as mesitylene and methyl substituted aromatics. Also, the reactions were carried out under ultrasonic irradiation for 8-11 hours followed by incubation for 4 days.

Based on our previous work on the utilization of boron trifluoride monohydrate as a readily available and significantly inexpensive alternative to triflic acid, we hypothesized that boron trifluoride monohydrate could be used for the protonation of sodium azide to generate aminodiazonium ion in situ which could then be used for the electrophilic amination of aromatics (Scheme 1).

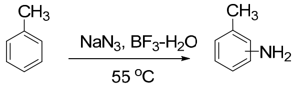


Scheme 1. Electrophilic amination of aromatics

Results and Discussion

At first, we prepared boron trifluoride monohydrate by bubbling boron trifluoride gas into distilled water in a Nalgene® bottle placed in a dry ice-acetone bath while swirling and shaking the bottle to mix the contents. When the weight of the complex started to remain constant at a weight corresponding to a ratio of 1:1 for the BF_3-H_2O complex, the process was stopped. Next we investigated the potential of the thus obtained thick, viscous and colorless liquid BF_3-H_2O complex to aminate aromatics.

Table 1. Optimization of reaction conditions for the amination of toluene with NaN_3 and BF_3-H_2O



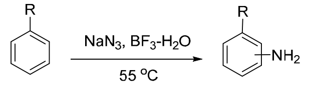
Entry	NaN_3 (equiv.)	$BF_3.H_2O$ (equiv.)	Toluene (equiv.)	Time (h)	Yield (%)*
a	1	10	2200	1	28
b	1	10	2200	2	39
c	1	10	2200	12	48
d	1	10	5	12	49
e	1	30	1	12	75#

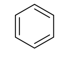
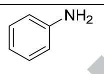
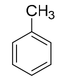
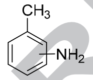
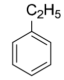
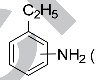
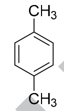
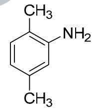
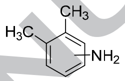
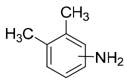
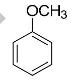
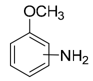
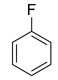
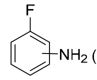
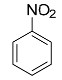
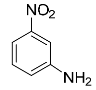
*Isolated yield based on NaN_3 used. #Isolated yield based on toluene and NaN_3 used.

Initially, we stirred NaN_3 in a large excess of toluene (2200 equiv.) in the presence of boron trifluoride monohydrate (10 equiv.) at 55 °C for an hour and were able to obtain the desired product toluidines in 28% yield (Table 1, Entry a). Longer reaction times improved the yield but the effect was not much pronounced (Table 1, Entry b, c). Even when a much smaller amount of toluene was used, the desired product was obtained in a comparable yield under the same conditions (Table 1, Entry d). Therefore, in the next experiment (Table 1, Entry e) we used an equimolar amount of toluene. However, we also increased the amount of boron trifluoride monohydrate by three fold so that it could act as a protic medium for the dissolution of the inorganic salt NaN_3, in addition to providing acidity required for the protonation of the azide anion. This time we were able to obtain the desired mixture of toluidines in 75% yield (Table 1, Entry e). The relative ratio of *ortho, meta* and *para* isomers of toluidine was 61:6:33, which is typical for electrophilic substitution reactions, as shown by ^1H NMR and GCMS analysis (Table 2, Entry b).

Various aromatic substrates were reacted with NaN_3 under similar reaction conditions. As shown in the summary of results in Table 2, alkyl benzenes reacted with NaN_3 to give the corresponding primary aromatic amines in good yield. Highly activated arene, anisole also reacted in good yield (Table 2, Entry f) with an *ortho*, *meta* and *para* isomer distribution ratio of 36:7:57. The amination of unsubstituted arene benzene gave aniline in a moderate yield (Table 2, Entry a). By contrast, highly deactivated arenes reacted only sluggishly. While fluorobenzene reacted to give the corresponding fluoroanilines, albeit in a low yield (Table 2, Entry g), only trace amount of nitroaniline was observed in the case of nitrobenzene even after prolonged heating (Table 2, Entries h). Therefore, as in other electrophilic amination procedures reported earlier,[28c,e;29] this amination procedure is not suitable for substrates that are strongly deactivated by electron withdrawing groups.

Table 2. Electrophilic amination of arenes with NaN_3 /BF_3-H_2O reagent system

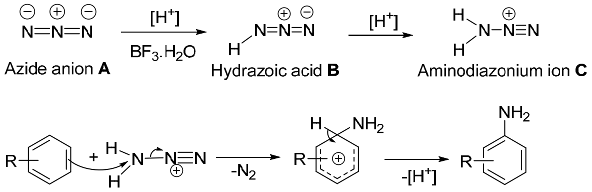


Entry	Arene	Time (h)	Product (*o:m:p*)^{i}	Yield (%)^{ii}
a		15		56
b		12	 (61:6:33)	75
c		12	 (53:0:47)	75
d		24		64
e		27	 (42:58)^{iii}	68
f		12	 (36:7:57)	76
g		14	 (21:6:73)	48
h		72		Trace

^{i}Isomer distribution determined by NMR and GCMS; ^{ii}Isolated yield based on arene used; ^{iii}2,3-Dimethylaniline: 3,4-Dimethylaniline

Nevertheless, our present protocol for primary aromatic amines via the direct amination of aromatics provides several advantages. In our present work, we have used sodium azide which is much more atom economical than the previously reported aminating agents such as hydroxylammonium choride,[26] hydroxylamine salts,[27a] hydroxylamine-O-sulfonic acid,[27c,d] and trimethylsilyl azide.[28c,e] Unlike these previous reports, which used an excess of aromatics, in our present research we have used the aminating agent and the aromatics in an equimolar amount, while achieving decent yields of the products. Therefore, from the perspective of atom economy, our present work offers a viable alternative to the previously reported direct amination of aromatics. Boron trifluoride monohydrate can be prepared in the laboratory by a simple procedure from boron trifluoride and water. As an easy to prepare efficient non-oxidizing Brønsted acid catalyst with sufficient acidity required for the reaction, boron trifluoride monohydrate offers a readily available and significantly inexpensive alternative to triflic acid which was previously used in the direct amination of aromatics.[28e,29] It also provides a metal free alternative to previously used metal based solid acid $AlCl_3$.[27d] In our reactions, boron trifluoride monohydrate also acts as an effective protic solvent for the sodium azide, an inorganic salt. Thus, by avoiding the use of organic solvents, the use of boron trifluoride monohydrate reduces waste-generation and makes the reaction environmentally friendly.

The direct amination of aromatics with NaN_3 in the presence of boron trifluoride monohydrate can be presumed to undergo through a mechanism similar to the one proposed by Olah and co-workers in earlier studies.[28c] In boron trifluoride monohydrate, which acts as a strong Brønsted acid system and provides superacidic stable ion conditions, protonation of azide **A** forms hydrazoic acid **B** in situ that undergoes further protonation to form aminodiazonium ion **C**. The aminodiazonium ion acts as the nitrenium ion "NH_2^+" source, which drives subsequent "NH_2^+" electrophilic addition to the aromatic substrate with the elimination of nitrogen, a facile leaving group (Scheme 2). Therefore, the nitrenium ion "NH_2^+" formed by the elimination of nitrogen from aminodiazonium ion can be envisaged as the reactive species, as also presumed by Borodkin and co-workers.[29]



Scheme 2. Formation of aminodiazoium ion and electrophilic amination

Conclusion

We have described an effective protocol for the synthesis of primary aromatic amines directly from aromatics by using sodium azide in the presence of boron trifluoride monohydrate. Boron trifluoride monohydrate acts as strong acid catalyst as well as an effective solvent for sodium azide providing sufficient acidity for the protonation of azide ion for the generation of hydrazoic acid and subsequently the aminodiazonium ion which acts as the nitrenium ion "NH_2^+" source for electrophilic amination of aromatics to give primary aromatic amines. Unlike previous reports of electrophilic amination of aromatics which used an excess of aromatics, in our reactions both the aminating agent and the aromatic substrate are used in equimolar amounts. Our study also demonstrates that for the purpose of electrophilic amination, easily accessible, nonoxidizing and inexpensive boron trifluoride monohydrate can be used as an effective substitute for expensive super acids such as triflic acid.

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Supplementary Data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.....

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